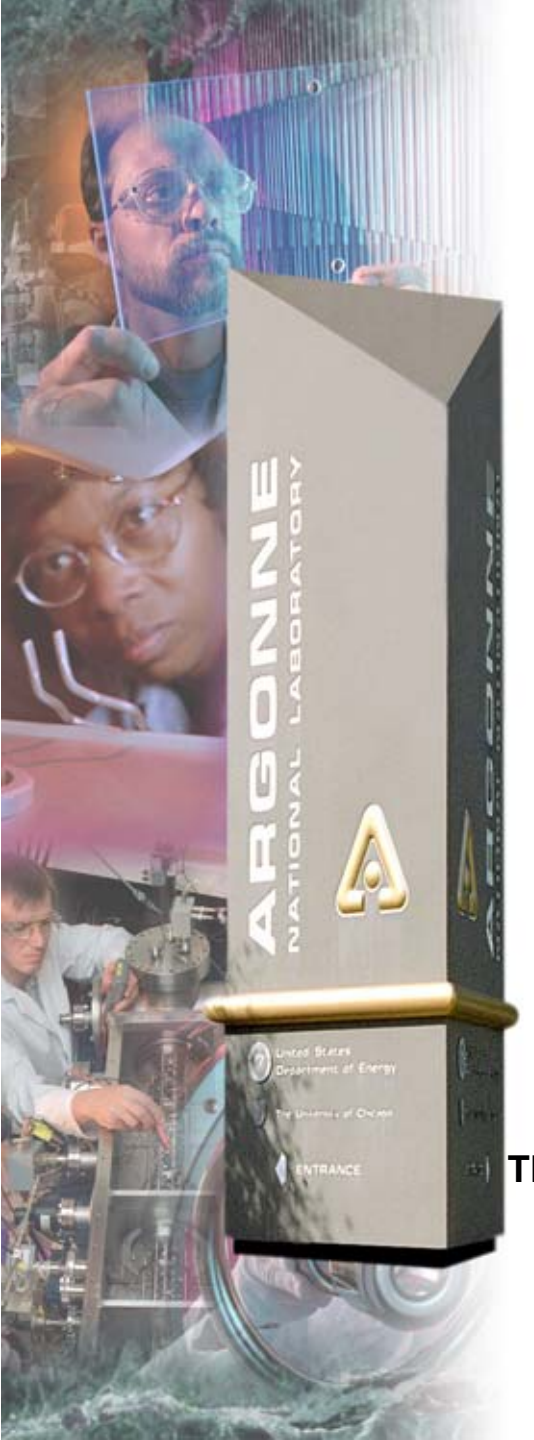

Catalysts for Autothermal Reforming

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Electrochemical Technology Program
Argonne National Laboratory

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This presentation does not contain any proprietary or confidential information

Hydrogen, Fuel Cells, and Infrastructure Technologies
Office of Energy Efficiency and Renewable Energy
U.S. Department of Energy

Objectives

- **To develop advanced fuel processing catalysts that meet DOE performance requirements**
  - Compared to Ni-based steam reforming catalysts, these new catalysts will
    - be able to process complex fuel mixtures, such as gasoline
    - process these fuels at higher rates
    - be more resistant to coking and sulfur poisoning
  - Improve our understanding of reforming reaction mechanisms, catalyst deactivation, and sulfur poisoning
  - Define operating parameters (e.g. air:fuel and steam:fuel ratios, temperature, gas hourly space velocities (GHSV), catalyst geometry) to optimize catalyst performance and lifetime

Budget, technical barriers and targets

- **FY204 Funding: $400K**
- **Technical barriers for hydrogen production**
  - A. Fuel Processor Capital Costs
  - G. Efficiency of Gasification, Pyrolysis, and Reforming Technologies
  - Z. Catalysts
- **Technical targets for reforming catalysts**
  - gas-hourly space velocity (GHSV) ≥ 200,000 h^{-1}
  - conversion ≥ 99.9% with H_2 selectivity ≥ 80%
  - lifetime > 5000 h
  - cost <$5/kWe

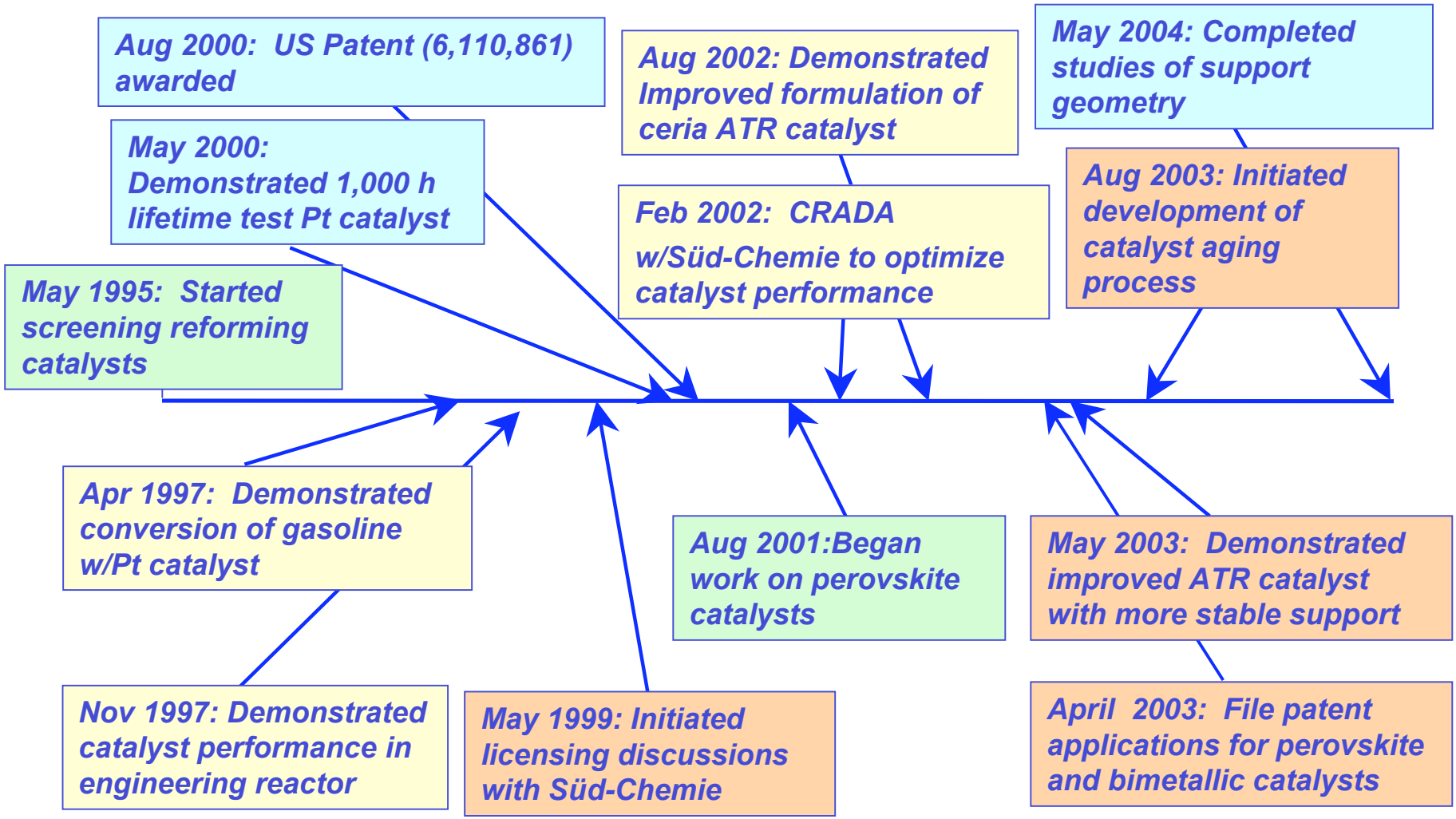
Approach

- Building on past ANL experience, we are investigating two classes of materials
  - transition metal(s) supported on oxide substrates
  - perovskites
- Determine catalyst performance (H_2 yield, CO_x selectivity, hydrocarbon breakthrough, fuel conversion) and stability as a function of:
  - catalyst composition
  - fuel composition and sulfur content
  - operating parameters: O_2:C and H_2O:C ratios, temperature, GHSV
- Conduct catalyst characterization and mechanistic studies to identify
  - factors influencing activity and selectivity
  - causes of deactivation
  - how sulfur affects catalyst activity

Project safety

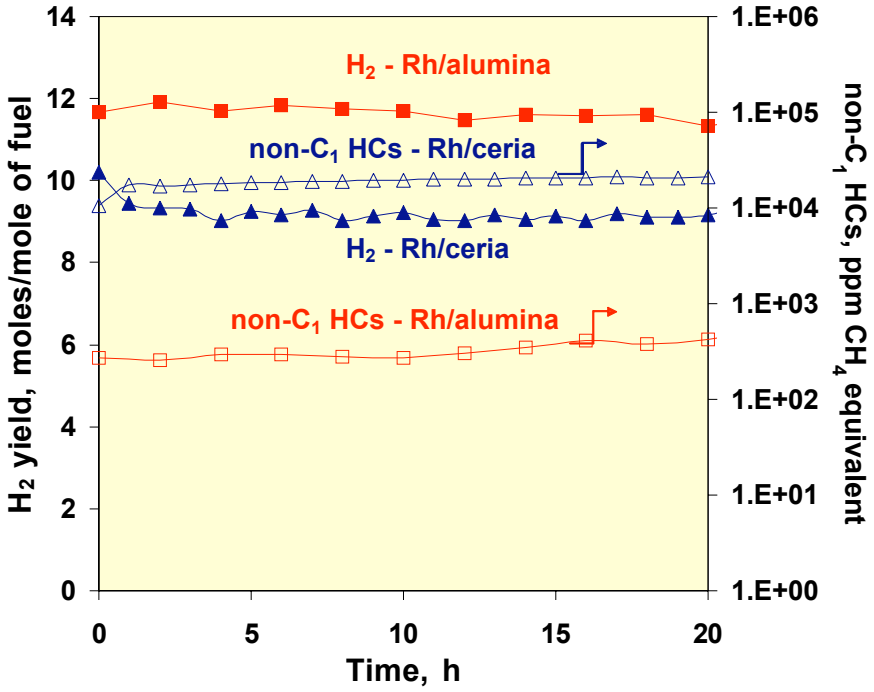
- **Internal safety reviews are performed for all aspects of this project to address ESH issues**
  - **Catalyst synthesis**
    - Synthesis procedures are performed in fumehoods to exhaust vapors of powders and solvents
    - Waste chemicals are collected and disposed of through the Laboratory's Waste Management Operations
  - **Microreactor systems**
    - Located in fumehoods
    - Equipped with safety interlocks that shut the system down if excessive temperature or pressure is sensed or the fumehood ventilation fails
- **Safety reviews are updated and renewed annually**

Project timeline

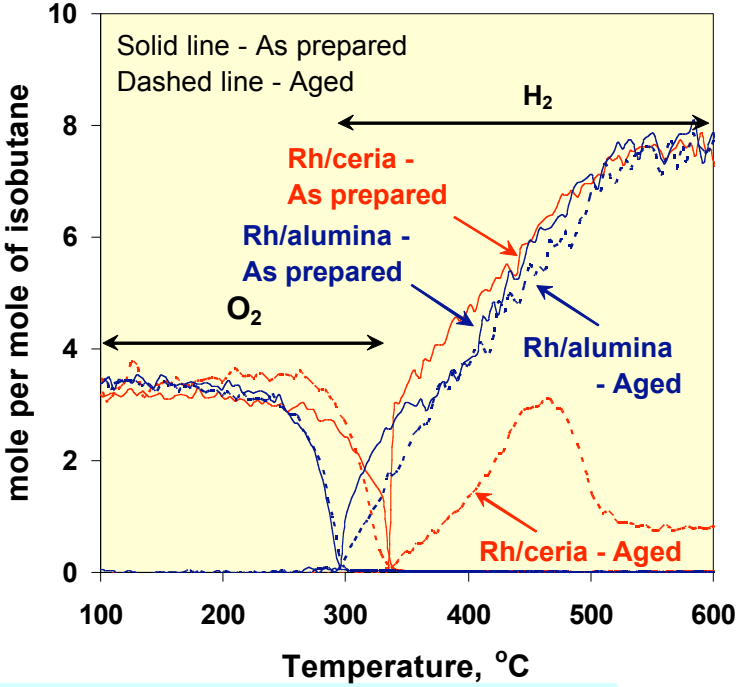


Refractory oxides provide a more stable support for Rh than reducible oxides

- **Higher H_2 yield and lower hydrocarbon breakthrough with Rh/alumina for gasoline ATR**



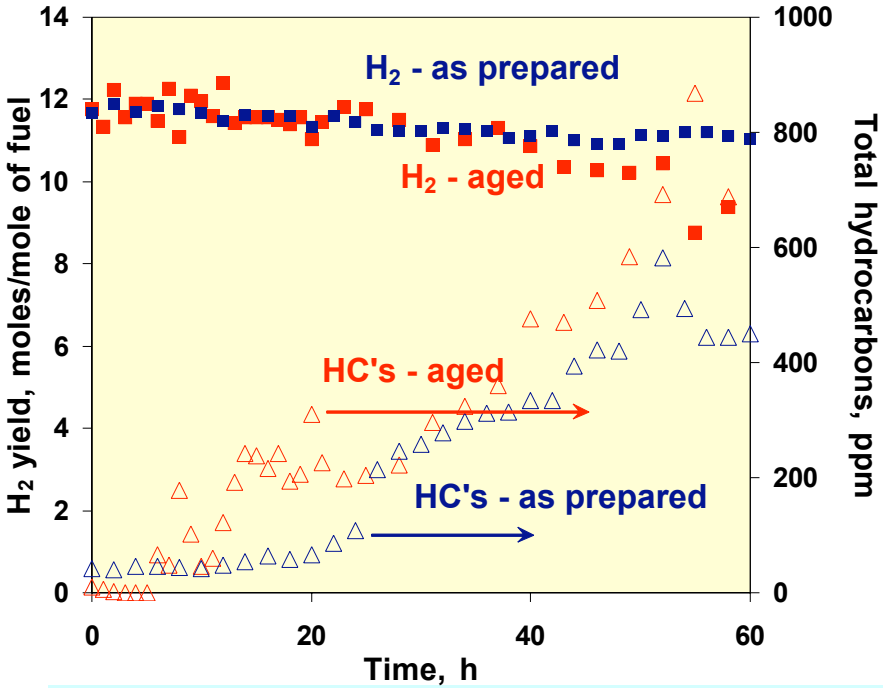
- **Significant decrease in H_2 yield with Rh/ceria but not with Rh/alumina after aging* for isobutane ATR**

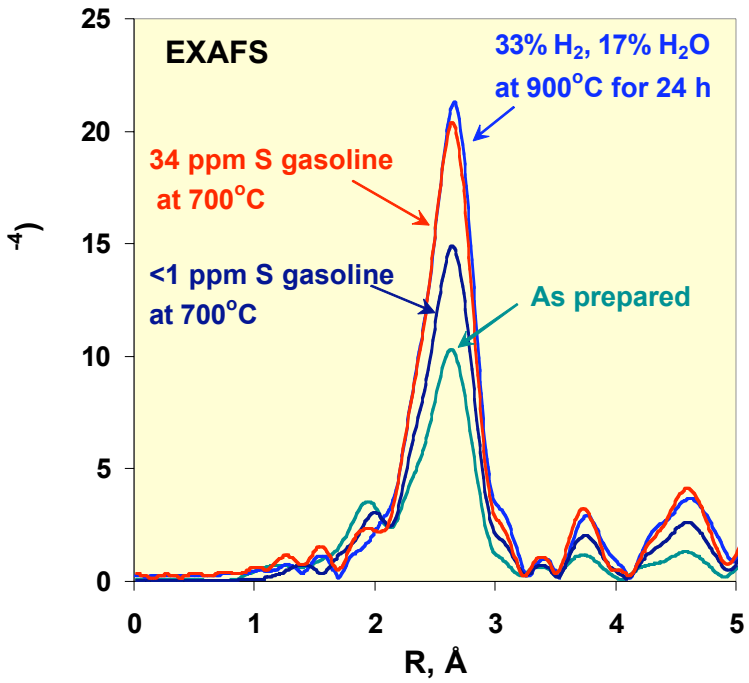


	Surface Area, m^2/g		Rh dispersion, %	
	Fresh	Aged*	Fresh	Aged*
Rh/alumina	130	105	81	31
Rh/ceria	36	3	21	1

* - treated at 900°C in H_2/H_2O for 24 h

We are working to develop an aging process to simulate effects of long-term operation



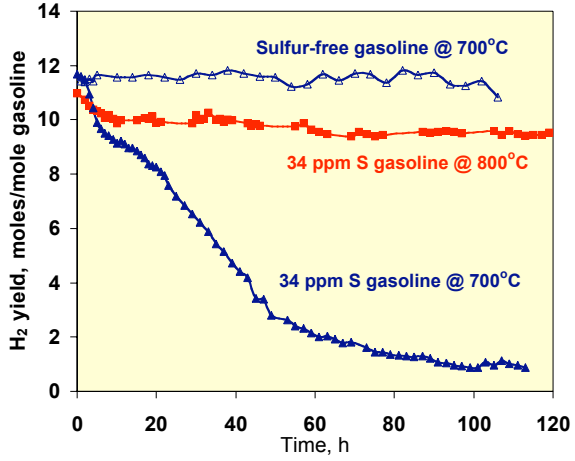


Rh dispersion, %

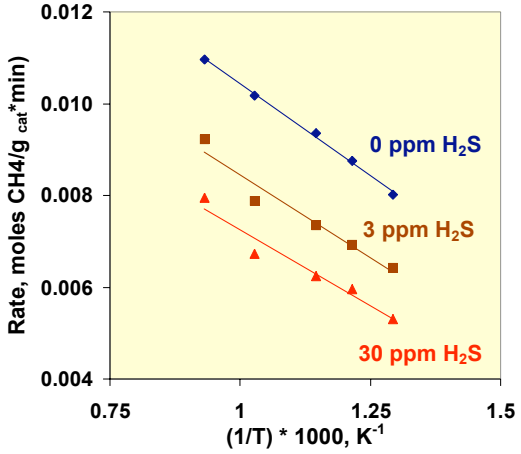
Catalyst	Initial	Reoxidized
As prepared	81	
33%H_2, 17% H_2O at 900°C - 24 h	31	
<1 ppm S gasoline at 700°C - 100 h	24	28
34 ppm S gasoline at 700°C - 100 h	3	13

Reversible adsorption of sulfur appears to be the primary cause of sulfur poisoning with Rh

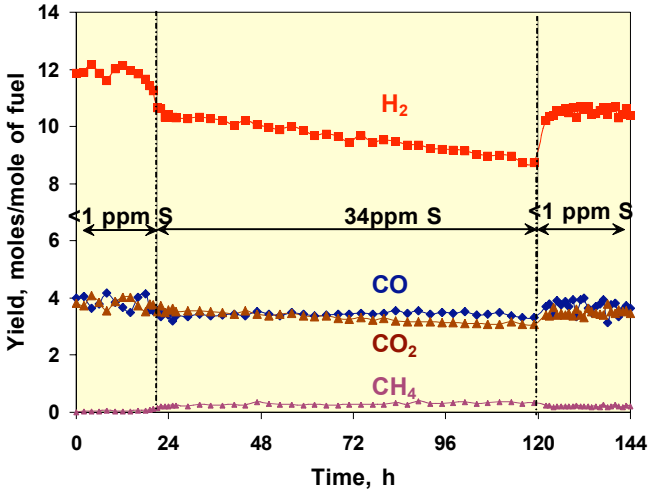
- **Effect of sulfur poisoning decreases with increasing temperature**

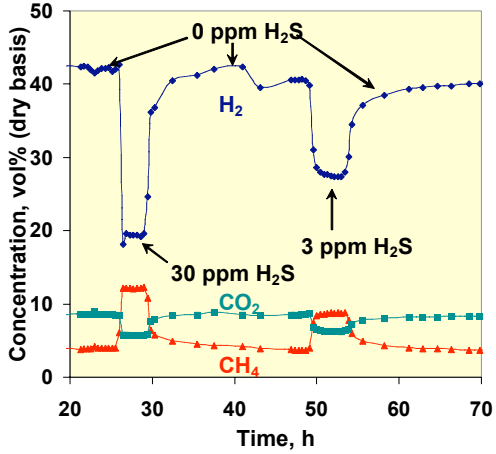


- **Loss in activity increases as H_2S concentration increases**



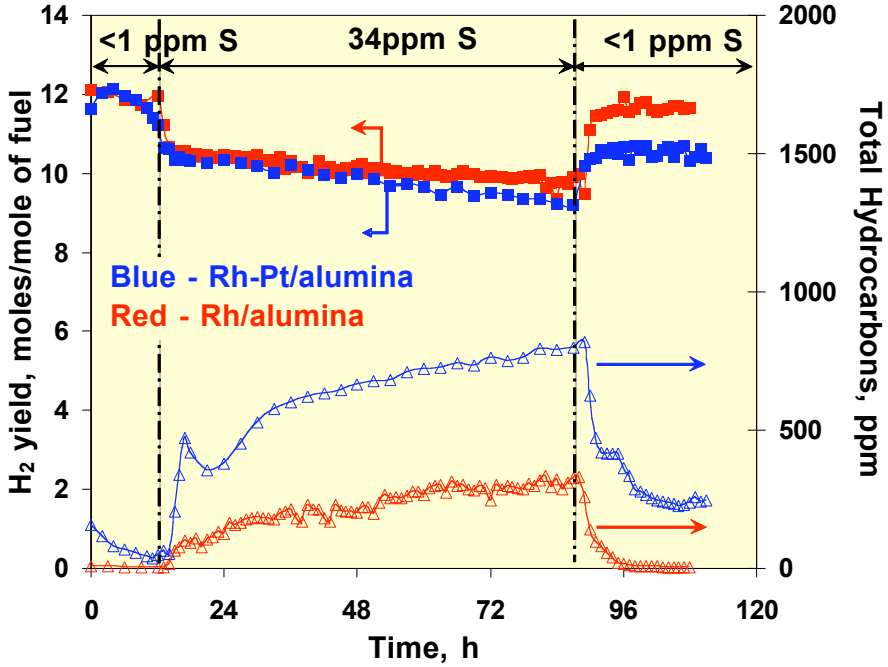
- **Most of the activity is recovered in ~1-2 h after sulfur is removed from feedstock**

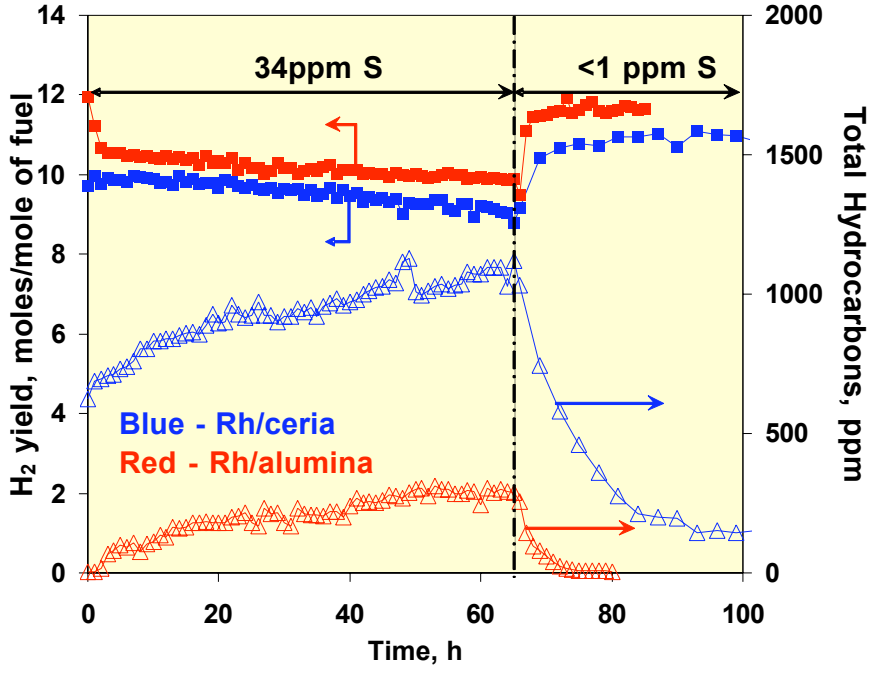




Use of bimetallic formulations or sulfur-adsorbing supports has not improved the sulfur tolerance of Rh

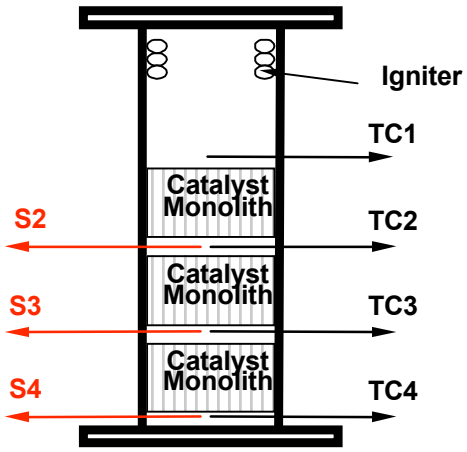
- The addition of a second metal is known to improve the sulfur tolerance of some catalysts, such as the addition of Pd to Pt catalysts used in petroleum refining
- Some supports, such as ceria, form a stable sulfide in the temperature range of ATR, which could serve as a potential "sink" for sulfur



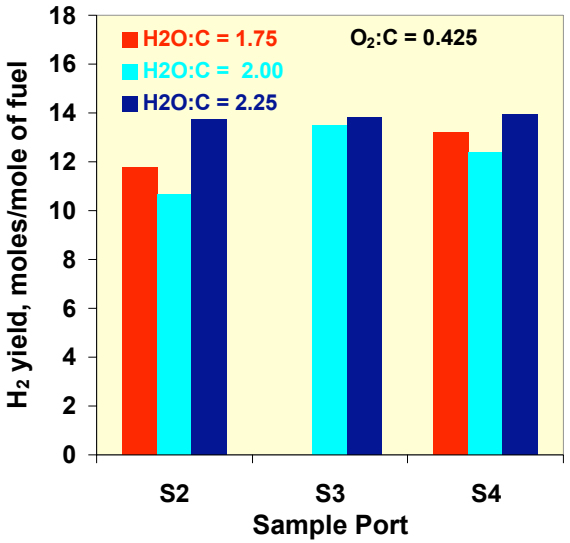


Proper selection of the structured support is critical for optimizing catalyst performance

- **Performance of a Rh catalyst loaded onto 600-, 900-, and 1200-cpi monoliths and a 40-ppi metal foam for reforming gasoline is being evaluated to determine optimal support geometry**
- **Some preliminary observations**
  - The highest temperature is observed at the exit of the first monolith
  - Nearly all of the H_2 is produced in the first monolith
  - CH_4 yield increases from the first to last monolith suggesting that methanation may be occurring as temperature decreases
- **Data are being used to generate a reaction model**

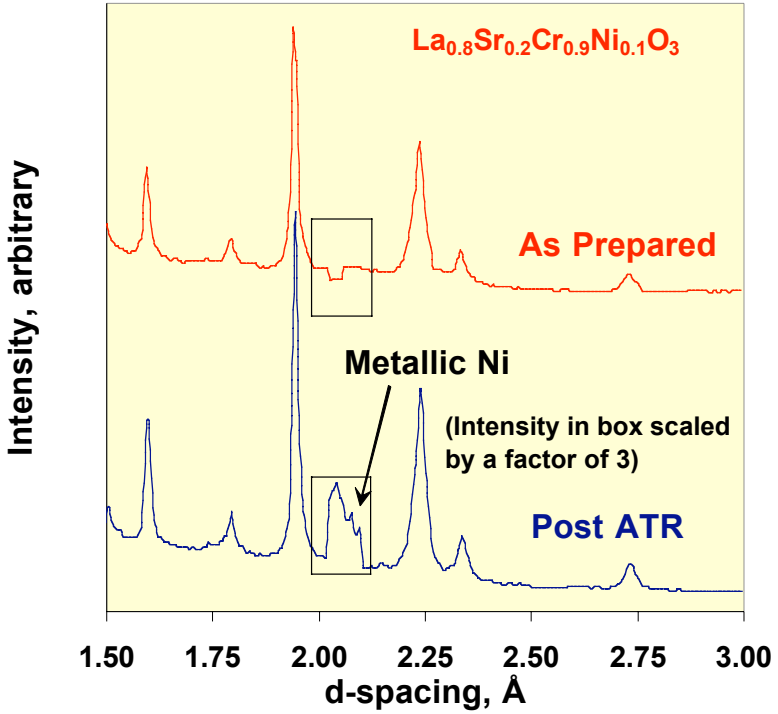


kW_e Reactor System

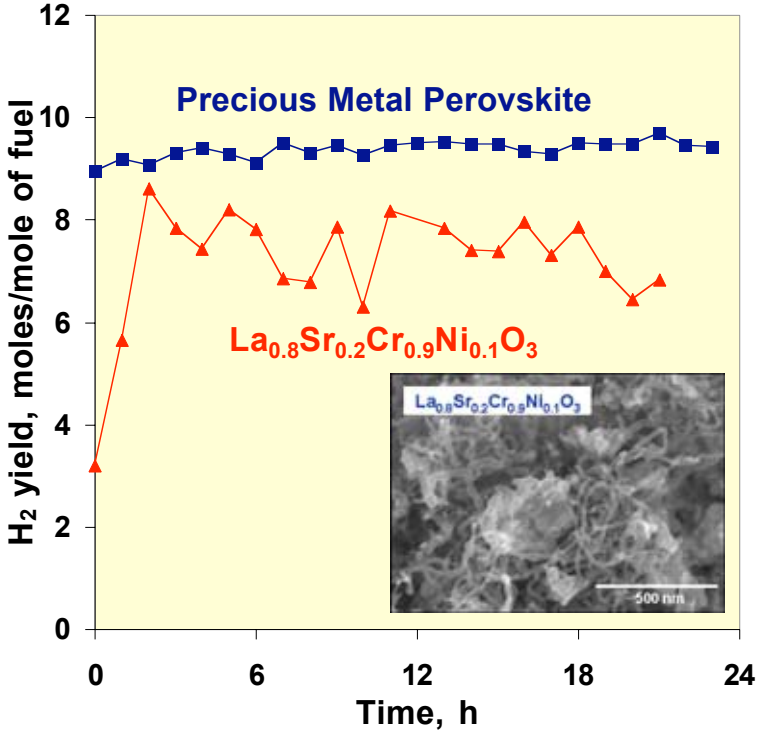


Less focus on perovskite catalysts

- Stability of Ni perovskite during ATR is an issue
- Results from electron microscopy and X-ray diffraction were inconclusive
- Neutron spectroscopy showed that metallic Ni particles was present



- Ni perovskites were active for gasoline ATR but the H_2 yield was low and decreased with time due to coking
- Substituting a precious metal for Ni produced a higher and more stable H_2 yield



Interactions and collaborations

- **University and industrial interactions**
  - University of Alabama (Prof. Ramana Reddy) to characterize ATR catalysts using SEM, TEM, and XPS
  - University of Alabama (Prof. Alan Lane) to develop more sulfur tolerant ATR catalysts
  - University of Puerto Rico, Mayagüez (Prof. Jóse Colucci) to determine operating parameters for reforming gasoline and biodiesel
  - Participant in a proposal with General Electric and University of Minnesota submitted in response to the Hydrogen Production and Delivery Research Solicitation
  - Süd-Chemie, Inc., monolith and foam studies

Response to reviewers' comments from FY03

- More emphasis on sulfur tolerance
- Need more fundamental understanding of reaction and deactivation mechanisms
- What criteria can be used to decide when a catalyst is "good enough"
- Interaction with reforming work in the Hydrogen Program

Milestones

Milestone	Date
Determine the optimal support structure (monolith vs. foam) to minimize mass transfer effects	01/04 (05/04)
Complete benchmarking of the ANL ATR catalyst against other reforming catalysts under development	05/04
Complete 1000 h test with best catalyst formulation supported on structured support using 30 ppm sulfur gasoline	09/04

Future work

- **Improve catalyst durability and minimize deactivation**
  - Conduct characterization studies of spent catalysts to further understanding of deactivation mechanisms
  - Validate catalyst aging process
  - Conduct long-term testing of improved catalyst formulations
- **Improve sulfur tolerance of catalysts by increasing our understanding of sulfur poisoning mechanisms**
- **Mechanistic studies to increase our understanding of reaction pathways**
- **Address catalyst issues identified in "FASTER" Program**
  - Catalyst deactivation and structural stability issues (i.e., effect of frequent and rapid startup)
  - Obtain performance data as a function of operating parameters to develop ATR/SR reaction models